

Transformation State of Archaeological Iron Oxides by Mössbauer Spectroscopy

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1. Introduction

Iron oxides are among the most informative mineral phases found in archaeological materials, including ceramics, pigments, and corrosion products. Their mineralogical and magnetic characteristics are influenced not only by ancient manufacturing processes, such as firing temperature and redox conditions, but also by long-term environmental alteration during burial. As a result, the present state of an archaeological iron oxide reflects the cumulative effects of both technological production and post-depositional transformation rather than a single formation event.

Conventional analytical techniques, such as X-ray diffraction and Raman spectroscopy, are effective for phase identification but often have limited ability to resolve poorly crystalline, nanosized, or superparamagnetic iron oxides. Mössbauer spectroscopy overcomes these limitations by providing atomic-scale information on iron oxidation state, magnetic ordering, and local structural environments, enabling more detailed interpretation of transformation processes. In this study, we introduce the concept of a Transformation State for archaeological iron oxides. Instead of interpreting individual mineral phases independently, Mössbauer hyperfine parameters are integrated to represent the overall transformation state of a material. This concept provides a basis for evaluating the combined effects of thermal evolution and environmental alteration, offering a more comprehensive approach to reconstructing the history of archaeological materials.

2. Transformation-State Concept

Rather than interpreting individual iron oxide phases separately, archaeological iron oxides are regarded as existing in a continuous transformation state reflecting their cumulative physicochemical evolution. The transformation state is represented using Mössbauer hyperfine parameters, including magnetic hyperfine field (H_{hf}), isomer shift (δ), quadrupole splitting (ΔEQ), relative spectral area, and magnetic phase fractions. These parameters collectively describe the degree of thermal transformation and environmental alteration recorded in archaeological materials.

3. Transformation-State Indices

The transformation state is quantitatively expressed using two complementary indices. The Thermal

Transformation Index (TTI) reflects magnetic ordering and crystallization based on H_{hf}, sextet fraction, and crystallinity. The Environmental Transformation Index (ETI) represents hydration and post-depositional alteration using δ, ΔEQ, doublet fraction, and environmentally sensitive FeOOH phases such as ferrihydrite, goethite, lepidocrocite, and akaganeite. Each archaeological sample is represented as a coordinate in a two-dimensional transformation-state space, enabling direct comparison of technological and environmental histories.

4. Transformation-State Mapping

The transformation state of archaeological iron oxides is represented in a two-dimensional state space using two complementary descriptors: the Thermal Transformation Index (T) and the Environmental Transformation Index (E).

For each sub-spectra i

$$H_i, \delta_i, Q_i = |\Delta EQ_{i,j}|, A_i \quad (1)$$

H_i : Magnetic Hyperfine field

δ_i : Isomer shifts

Q_i : Absolute quadrupole splitting

A_i : Relative spectral area

The noemalized area fraction is

$$a_i = \frac{A_i}{\sum_{j=1}^n A_j} \quad (2)$$

The transformation state is then expressed conceptually as

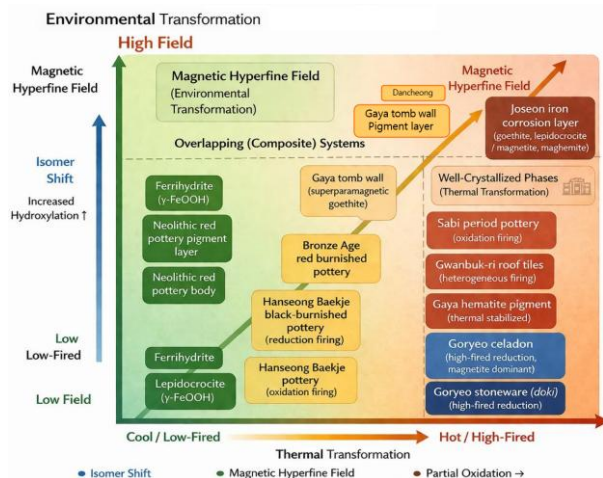
$$TS=f(H_i, \delta_i, Q_i, R_i) \quad (3)$$

$$TS=(T,E) \quad (4)$$

where T reflects the degree of thermally induced crystallization and magnetic ordering, while E represents environmental alteration associated with hydration, oxidation, and burial processes. Each archaeological material is assigned a unique coordinate according to its Mössbauer-derived transformation state, allowing direct comparison of technological and post-depositional histories.

Unlike conventional phase classification, the proposed transformation-state map visualizes archaeological materials as continuously evolving systems rather than discrete mineral assemblages. This approach enables transformation pathways to be

interpreted in terms of thermal processing and environmental overprinting, providing an intuitive framework for comparing different archaeological materials.



Environmental Transformation Axis (↑)

- Hydration / Hydroxylation increase
- Poor crystallinity
- FeOOH (ferrihydrite, lepidocrocite, goethite)
- Superparamagnetism increase
- Isomer shift increase

Thermal Transformation Axis (→)

- Firing temperature increase
- Crystallinity increase
- Dehydration / Dehydroxylation
- Magnetic ordering increase
- Magnetic hyperfine field increase

Fig. 1 Results of Mössbauer parameters

The proposed transformation-state concept provides a unified framework for interpreting the thermal and environmental histories of archaeological materials. Beyond conventional phase identification, it enables systematic comparison of firing conditions, weathering, corrosion, and burial processes across different materials. Future applications include the development of standardized transformation-state databases, integration with complementary analytical techniques, and AI-assisted classification of archaeological materials based on Mössbauer-derived transformation states. This approach may contribute to more objective reconstruction of ancient manufacturing technologies and support scientific decision-making in cultural heritage research and conservation.

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